Genesis of PGE-polymetallic deposits in lower Cambrian black rock series, southern China: Evidence from fluid inclusion and inert gas isotopic studies

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Abstract. Microthermometric measurements of fluid inclusions in the PGE-polymetallic deposits hosted in the Lower Cambrian black rock series in Southern China were performed, and two types of fluid inclusions were identified. Type I are of NaCl-H_2O system with low to medium salinity, and their homogenization temperatures (Th) and salinities are 106.9 ~ 286.4°C and 0.8 ~ 21.8 wt% NaCl eq. respectively; Type II are of $CaCl_2$-NaCl-H_2O system with medium - high salinity, and their Th and salinities ranging from 120.1 to 269.6°C and 11.4 to 31.4 wt% NaCl eq. Characteristics of fluid inclusions in the PGE-polymetallic ores and carbonate-quartz stockworks in the underlying phosphorites are nearly the same, that they may represent the ore-forming fluid of main metallogenetic stage. The mode value of Th of those fluid inclusions is about 170°C, while their salinities possess a remarkable bimodal distribution pattern with two modal values of 27~31 wt% NaCl eq. and 4~6 wt% NaCl eq.; Inert gas isotopic analyses combined with microthermometric measurements of the fluid inclusions suggest that the ore-forming fluids of main metallogenetic stage were probably formed by mixing of basinal hot brine with $CaCl_2$-NaCl-H_2O system and seawater with NaCl-H_2O system. Finally, a new metallogenic model is proposed.

Keywords. Fluid inclusion, basinal hot brine, inert gas isotopes, PGE-polymetallic deposits in black rock series, Southern China

1 Introduction

Ni, Mo, V, Cu, U, Ba, rare earth elements (REE) and specially platinum group elements (PGE) are extraordinarily enriched in the Lower Cambrian black rock series of Yangtze Platform in Southern China, and locally formed a new type of PGE deposit – Ni-Mo-PGE deposits or ore spots, within which Zhangjiajie and Zunyi are the most representative ones (Coveney and Chen 1991; Coveney et al. 1992; Mao et al. 2001; Wang et al. 2004). There exist three major opinions on the genesis of this kind of deposit: normal seawater sedimentary model (Fan 1983; Mao et al. 2002), submarine exhalative hydrothermal deposition model (Coveney and Chen 1991; Coveney et al. 1992; Li et al. 2000; Lott et al. 1999) and multi-stage metallogenic model (Zhang et al. 2002).

2 General geology of the ore deposits

Precious metals such as PGE are predominantly occurred in the Cambrian Ni-Mo-PGE bearing black shale ore layers. The thickness of the ore layers is usually 20~30cm, locally 50~80 cm. Observations under microscope show that the ores are mainly composed of clay mineral, feldspar, quartz, carbonate mineral, organic matter, jordisite and pyrites. Pyrite, one of the most important ore minerals in diameter of 1~5 mm, mainly occurred as laminated and lentiform, occasionally disseminated structures. Quartzes are of fine-grained and anhedral crystals in diameter as large as 50 μm. Carbonate minerals occur as microgranules or micritic aggregates with greatly-varied diameters.

In the underlying Cambrian phoshorites of the Ni-Mo-PGE bearing black shale ore layers in Daping deposit of Zhangjiajie in Hunan Province, many stockworks with a thickness of several millimeters were recognized, which filled with carbonate minerals and quartzes and vertically cut the strata.

3 Microthermometric measurements

There are quite a limited number of fluid inclusions in quartz and carbonate minerals in PGE-polymetallic ores, the size are usually <5μm and mostly 2~3μm, occasionally 10μm; the vapor/liquid ratio is about 10%~20%, occasionally 30%; For comparison, numerous fluid inclusions are found in carbonate-quartz stockworks in phosphorites underlying the ore layer, the sizes are usually 2~3μm and smaller than those in the ores; The gas/liquid ratio is 10~30%, occasionally 50%.

150 data pairs of Th and salinities of primary and pseudosecondary fluid inclusions were collected in this study. Based on compositions and phases in fluid inclusions, two types of inclusions were recognized in this study: Type I with NaCl-H_2O system and low salinity; Type II with $CaCl_2$-NaCl-H_2O system and medium to high salinities.

Microthermometric measurements demonstrated that the freezing temperatures of the type I inclusions were -57~-45°C, and their Teu (the eutectic point of NaCl-H_2O aqueous system) and Tm were about –21°C°Cand -13.9~-0.5°C respectively. The freezing temperatures of type II inclusions were commonly -83°C~-58°C, and the initial melting started when the inclusions slowly heating to the temperature -55~-52°C, the initial melting of the liquid phase started and vapour bubbles started to

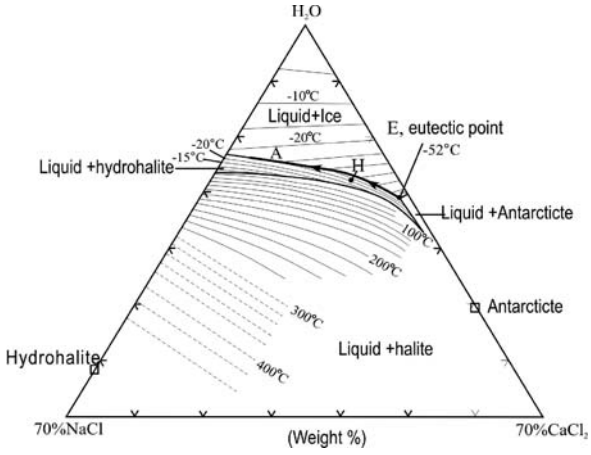

Figure 1: Phase diagram of $CaCl_2$-NaCl-H_2O system in fluid inclusion (after Shen et al 2003).

bounce about gently. Thus, the equilibrium eutectic point of type II inclusions, which is the eutectic melting point of $CaCl_2$-NaCl-H_2O aqueous system shown on the point E in Figure 1, can be estimated to be = -52°C. During the following, heating the liquid phase moved along EA-cotectic line of ice and hydrohalite (NaCl·$2H_2O$) on Figure 1. When the rising temperature reached -34.3 ~-24°C, the ice crystals in the inclusions gradually melted. The hydrohalite (NaCl·$2H_2O$) in the fluid inclusions melted completely between-27.5°C and -14.1°C during continuously heating. The point of liquid phase left the cotectic line and moved toward the point of the hydrohalite on the NaCl-H_2O boundary, until intersecting the isotherm line of the dissolved hydrohalite. Points of intersection represent the compositions of the liquid phase. For the inclusions whose ice crystal and hydrohalite melted at -34.3°C and -27.5°C separately, its corresponding composition consisting of 8%NaCl, 22%$CaCl_2$ and 70%H_2O (H on Fig. 1) and the apparent salinity is 30 wt% NaCl eq.

4 Analytical results and discussion

Th of fluid inclusions from the PGE poly-metallic ore are 106.9~286.4°C, with a mode value of 160~170°C; those in carbonate-quartz stockworks in phosphorites are 120.1~256.8°C, with a mode value of about 170°C, suggesting that the Th of fluid inclusions in the ores and the stockworks are quite similar, and their Th represent the ore-forming fluid's temperatures of main metallogenic stage.

Salinities of fluid inclusions in the ores are 0.8~33.4 wt% NaCl eq. and possess a remarkable bimodal distribution pattern with mode values of 30~32 wt% NaCl eq. and 4~6 wt% NaCl eq., the densities are 0.730~1.035g/cm^3; The salinities and the densities of fluid inclusions in carbonate-quartz stockworks in phosphorites are 4.2~30.6 wt% NaCl eq. and 0.870~1.068 g/cm^3 respectively, and the former also shows a remarkable bimodal distribution pattern with mode values of 27~28 wt% NaCl eq. and 4~6 wt% NaCl eq. The measured results demonstrate that the salinities and the densities of fluid inclusions in the PGE-polymetallic ores are similar to those of the underlying carbonate-quartz stockworks, that they may be used to represent those of the ore-forming fluid of main metallogenic stage.

Lott et al. (1999) had observed coexistence of fluid inclusions enriched in gaseous phases with those in liquid phases in PGE-polymetallic ores, and thought that boiling might have been occurred during metallogenisis. We found no evidence of coexistence in the samples that we studied, but detailed observation of fluid inclusions let us believed that mixing of different fluids might have been occurred during ore-forming process, the evidence include: The greatly varied gas/liquid ratios varying between 5% to 40%; Coexistence of pure aqueous and nearby gas-liquid phases fluid inclusions in the carbonate-quartz stockwork in phosphorite (Fig. 2A); Concomitance of fluid inclusions with a $CaCl_2$-NaCl-H_2O system (medium-high salinities) and those with a NaCl-H_2O system (low-medium salinities) in the PGE-polymetallic ores (Fig. 2B). These observations imply that mixing between brine with a medium-high salinity and fluid with a low to medium salinity might have been occurred in the formation of the PGE polymetallic ores. The bimodal distribution patterns of salinities mentioned above may reflect fluid mixing.

He-Ar isotopic compositions of fluid inclusions trapped in pyrites in the PGE-polymetallic ores were systematically analyzed by using an inert gas isotopic mass spectrometer, and the results indicate show that the ore-forming fluids possess low $^3He/^4He$ ratios, ranging from 0.43×10^{-8} to 26.39×10^{-8}, with corresponding R/Ra ratios of 0.003~0.189 (R represents the real $^3He/^4He$ value of samples, and Ra represents the $^3He/^4He$ ratios of atmosphere, usually 1.4×10^{-6}); The $^{40}Ar/^{36}Ar$ ratios 258 ~ 287, closing to these of the air-saturated water. He-Ar isotopic studies indicate that the ore-forming fluids were mainly composed of formation water or basinal hot brine and air-saturated water (sea water), the content of mantle-derived fluid or deep-derived magmatic water might be negligible (Sun et al. 2004). The inert isotopic analyses provided evidences for the fluid mixing in the metallogenetic process from another aspect.

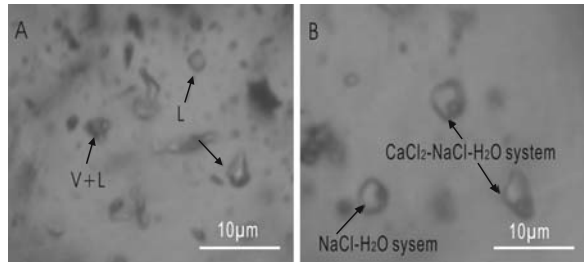

Figure 2: Coexisting fluid inclusions expressed for fluid mixing.

5 New metallogenic model

In the Early Cambrian, the basinal hot brine trapped in the Caledonian basins, which were distributed along southern margin of South China Craton and accumulated giant thick sediments, was expelled and migrated laterally along strata because of the pressure caused by overlying sediments. The basinal hot brine absorbed Ni, Mo, V, PGE from the around rocks and transformed to be ore-bearing hydrothermal fluids with $CaCl_2$-NaCl-H_2O system and medium-high salinity, then ascended along faults and mixed with sea water of NaCl-H_2O system, and finally formed PGE-polymetallic deposits or spots in the black rock series during the Early Cambrian (541.3±16Ma, Mao et al. 2001). The nearly vertical carbonate and quartz filled stockworks underlying the ore layers probably represent remains of ascending channel-way of the basinal hot brines.

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References

Coveney RM Jr, Chen NS (1991) Ni-Mo-PGE-Au-rich ores in Chinese black shales and speculations on possible analogues in the United States. Mineralium Deposita 26: 83-88

Coveney RM Jr, Murowchick JB, Grauch RI (1992) Field relations, origins and resource implications for platiniferous molybdenum-nickel ores in black shales of South China. Exploration and Mining Geology 1:21-28

Li SR, Gao ZM (2000) Source tracing of noble metal elements in Lower Cambrian black rock series of Guizhou-Hunan Provinces, China. Science in China (Series D) 6: 625-632 (in Chinese with English abstract)

Lott DA, Coveney RM Jr, Murowchick JB (1999) Sedimentary exhalative nickel-molybdenum ores in South China. Economic Geology 94:1051-1066

Mao JW, Zhang GD, Du AD (2001) Geology, Geochemistry, and Re-Os isotopic dating of the Huangjiawan Ni-Mo-PGE deposit, Zunyi, Guangzhou Province-with a discussion of the polymetallic mineralization of basal Cambrian black shales in South China. Acta Geologica Sinica 2: 234-243

Shen K, Zhang ZM, Van Den Kerkhof AM(2003). An unusual high-density and saline aqueous inclusions from the ultra-high pressure metamorphic rocks in the Southern Su-Lu region, eastern China. Chinese Science Bulletin 10: 1076-1081

Sun XM, Wang M, Xue T, Ma MY, Li YH (2004) He-Ar isotopic systematics of fluid inclusions in pyrites from PGE-polymetallic deposits in Lower Cambrian black rock series, South China. Acta Geologica Sinica 2: 471-475

Trace Metals in Solving Petrogenetic Problem and Controversies. Augustithis, S.S. Ed, Athens: 447-474

Wang M, Sun XM, Ma MY (2004) Geochemistry of Ore-forming Fluid and Its Metallogenetic Significances of PGE-polymetallic Deposits in Lower Cambrian Black Rock Series, Southern China. Acta Scientiarum Naturalium Universitatis SunYatseni 5: 98-102 (in Chinese with English abstract)

Zhang GD, Li JL, Qiong QR(2002) Enrichments features and patterns of PGE metals in black shales from Zunyi area, Guizhou Province. Mineral deposit 4: 377-385 (in Chinese with English abstract)